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Vapor-phase sorption of hexachlorobenzene on typical municipal solid waste (MSW) incineration fly ashes, clay minerals and activated carbon

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ABSTRACT

Column sorption experiments were conducted at 330 °C and 250 °C to study the vapor-phase sorption of hexachlorobenzene (HCB) on two kinds of municipal solid waste (MSW) incinerator fly ashes, kaolinite, montmorillonite and activated carbon (AC). Both Freundlich equation and linear equation well fitted the sorption isotherms of HCB vapor on fly ashes and clay minerals at 330 °C ($r^2 > 0.87$), while the sorption isotherm of HCB vapor on AC at 330 °C was in the shape of Brunauer type-II adsorption. Catalytic dechlorination of HCB was found to occur on the surface of fly ashes, and pentachlorobenzene was the only dechlorination product detected in the effluent gas. Increasing temperature decreased the sorption of HCB vapor on fly ashes, and promoted the catalytic dechlorination of HCB. On the assumption that the organic carbon and clay minerals in fly ash were derived from AC, kaolinite and montmorillonite, the relative contributions of these components to the apparent sorption capacity of fly ashes at 330 °C were estimated. It was found that very small percentage of AC contributed the most to the apparent sorption of HCB vapor on fly ash. The sorption coefficient of HCB on montmorillonite at 250 °C was 37 times higher than that at 330 °C, suggesting montmorillonite could be a kind of low-cost sorbent to effectively reduce the emission of vapor-phase organochlorine compounds from MSW incinerators.

1. Introduction

Incineration is a viable management strategy for treating municipal solid waste (MSW) with economic benefits of separation and recycling, resource recovery in the form of heat and power production (McKay, 2002). However, polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs) and hexachlorobenzene (HCB), belonging to the category of persistent organic pollutants, can be formed in the incineration processes (Chi et al., 2006a). The emission abatement of these toxic organochlorine compounds in flue gas is growing in importance because of the serious environmental and health concerns (Everaert and Baeyens, 2002).

As the typical hydrophobic organic chemicals, organochlorine compounds produced in MSW incineration are inclined to be adsorbed on the surface of fly ashes (Hoffman et al., 1990; Castro-Jiménez et al., 2008). Lundin and Marklund (2005) found that PCDD/Fs in fly ash could even account for more than 90% of the total PCDD/Fs released from an incinerator. Previous studies demonstrated that vapor-phase sorption of organochlorine compounds on fly ash could be considered as a function of the properties of sorbents, the concentrations of pollutant and the operating temperature (Hoffman et al., 1990; USEPA, 1999).

Besides the residual carbon from incineration, the organic component of fly ash is derived from AC injected in MSW incineration systems to remove toxic organochlorine compounds from the flue gas (Chi et al., 2006b; Lin and Chang, 2008). The inorganic component of fly ash is consisted of plenty of clay minerals and a small amount of metal oxides (Eiceman et al., 1979; Karademir et al., 2004). Some metal oxides such as CuO, ZnO, and MnO, were found to have the ability to catalyze the dechlorination of PCDD/Fs and other organochlorine compounds at 250–450 °C (Stach et al., 1999; Weber et al., 2002b; Lundin and Marklund, 2007). It brought difficulties to the study of the vapor-phase sorption of organochlorine compounds on fly ash due to the interference of dechlorination process. To our knowledge, only a few studies (Mätzing et al., 2001; Everaert et al., 2003; Karademir et al., 2004; Chi et al., 2006b) have investigated the vapor-phase sorption of PCDD/Fs and dioxin-like PCBs on fly ash and their removal efficiencies. The actual contributions of fly ash components to its sorption capacity at high temperature are still not clear.

The objectives of this work were to conduct a quantitative description and theoretical interpretation of the underlying

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Abbreviations: MSW, municipal solid waste; GF-FA, grate furnace fly ash; FB-FA, fluidized bed fly ash.

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sorption mechanism of organochlorine compounds on MSW incineration fly ash at high temperatures, and to evaluate the relative contributions of fly ash components to the sorption capacity of fly ash. In the study, HCB was selected as a model compound of organochlorine compounds. Two clay minerals (montmorillonite and kaolinite) and AC (bamboo charcoal) were used to simulate the components of fly ash. A laboratory scale apparatus was adopted to investigate the vapor-phase sorption of HCB on two kinds of fly ashes from different sources and the contributions of their components. In addition, the effect of temperature on vapor-phase sorption of HCB was also investigated. Some conclusions are then drawn concerning the dominant parameter influencing the distribution of HCB between the vapor-phase and the solid-phase, hoping to provide theoretical evidence for emission abatement technology of organochlorine compounds in flue gas.

2. Materials and methods

2.1. Sorbents and their characterization

Two fly ash samples were collected from a grate furnace MSW incinerator (Zhejiang, China) and a fluidized bed MSW incinerator (Harbin, China), respectively. Prior to use, samples were sieved to less than 0.15 mm particle size, and then placed in a furnace at 300 °C for 17 h to remove HCB and other chlorinated benzenes. Bamboo charcoal was made by burning bamboo inside an oven at temperatures over 800 °C. Two typical kinds of clay minerals, montmorillonite (Chemical Pure, CP) and kaolinite (CP), were purchased from Damao Chemical Reagent Company (Tianjin, China).

The particle size distributions of test sorbents were measured by scanning electron microscopy (SEM, JSM-5600LV, Jeol, Japan). BET surface and pore size distribution were measured by BET nitrogen adsorption method (Nowa 4000, Quantachrome, USA). The chemical components of sorbents were analyzed by X-ray fluorescence spectrometry (XRF, Magix 601, Philips, the Netherlands) and Elemental Analyzer (Vario EL III, Elementar, Germany).

2.2. Sorption experiments

HCB (organic analytical standards) and 1,3,5-tribromonated benzene (purity 98%) were purchased from Shanghai Chemical Reagent Inc. (China) and Alfa Aesar (Britain), respectively. The vapor-phase sorption of HCB on fly ashes and their simulated components were studied by a laboratory scale sorption apparatus. The apparatus was schematically shown in Fig. 1. It mainly consisted of two furnaces, a U-tube with porous glass plate and a glass cartridge filled with XAD resin.

Certain amounts of HCB stock solution prepared in hexane were spiked in a quartz boat inside Furnace 1#. Nitrogen was used as sweeping gas with the velocity of 24 mL min^{-1}. A steady feed stream with vapor-phase HCB concentrations ranging from 0.56 mg N m^{-3} to 20 mg N m^{-3} could be acquired by regulating the temperature of Furnace 1# between 180 °C and 300 °C. 0.1 g sorbents (0.05 g for AC) were fed in the vertical stainless steel fixed-bed reactor (20 mm long × 4 mm i.d.) installed in Furnace 2# at the temperatures of 250 °C and 330 °C. Based on the results from preliminary kinetic studies, 30 min was selected as equilibrium time for vapor-phase sorption of HCB. On completion of the sorption experiment, HCB which was not adsorbed was trapped by 10 mL hexane (J.T. Baker, USA) in the U-tube with porous glass plate. Before discharging, a glass cartridge plugged with 10 g XAD-2 resin was used to prevent the emission of organic pollutants. 50 μg L^{-1} of 1,3,5-tribromonated benzene was spiked in the hexane solution as internal standard. The solution in the U-tube with porous glass plate was transferred to a glass vial and concentrated to 2 mL for instrumental analysis.

2.3. Instrumental analysis

HCB and its dechlorination products were analyzed on a gas chromatography (GC) instrument (HP 5890) equipped with a capillary DB-5 column (30 m × 0.25 mm i.d. × 0.25 μm film thickness, J&W Scientific, USA) and electron-capture detector (ECD) by internal standard method. Temperature program was as followed: maintain an initial oven temperature of 130 °C for 3 min, rise to 260 °C at the rate of 8 °C min^{-1} and keep 20 min. The detector temperature was 280 °C, and the injection port temperature was 260 °C. The GC was run in splitless mode, and the injection volume was 1 μL. N_2 was used as the carrier gas (1 mL min^{-1}).

2.4. Quality assurance and quality control

Several control measurements were performed. One gram of treated fly ashes was extracted by ultrasound with 5 mL toluene

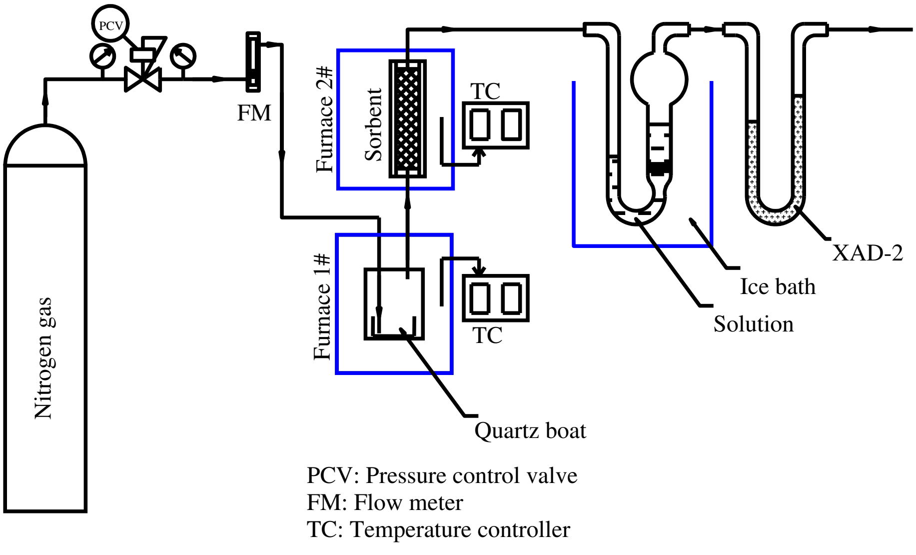

Fig. 1. Schematic diagram of HCB vapor sorption apparatus.